

### **Remarks**

Claims 3, 4, 6 and 7 are canceled.

Claims 1, 5, 8, 10 and 11 are currently amended.

Claims 1, 5 and 8-14 are now present in this application and are under consideration.

There are no allowed claims.

### **Amendments**

The present claims are amended to incorporate the limitations of claims 3, 4 and 7 into independent claim 1. Claims 3, 4 and 7 are canceled as redundant. Further, the 2-hydroxyphenylbenzotriazoles are now limited to those of formula IIa.

The definition of "y", second line from the bottom of amended claim 1, is from original claim 11.

Claims 5, 8, 10 and 11 are amended to depend on claim 1.

No new matter is added.

### **Claim Rejections**

Claims 1 and 3-13 are rejected under 35 USC 102(b) as anticipated by JP 9193322.

Applicant respectfully rebuts these rejections.

The Examiner requires some proof that the present high density polyethylene prepared with a Phillips catalyst is unique over polyethylene of the metallocene type.

Please find enclosed a copy of chapter 3, pages 21-28 of the Handbook of Polyolefins, edited by C. Vasile and R. B. Seymour, Marcel Dekker NY, 1993. The article summarizes the different catalysts used in polyolefin production. Special emphasis is given to the "Phillips type" catalyst, which contains at any rate chromium oxide often immobilized on a silica support.

"Metallocene" catalysts are generally more efficient and can be used in smaller amounts compared to "Phillips type" catalysts. For this reason they need not to be removed from the polymer. Usually the metallocene is a dicyclopentadienyl Zr or Ti derivative. Aluminumalkyl compounds are used as co-catalysts or activators. We have enclosed an article of I. S. Melaaen from Borealis A/S presented at the 2<sup>nd</sup> International Congress on Metallocene Polymers, Metallocenes '96, edited by Schottland Business Research Inc, 1996 page 87-95 with the title: "From Chromium to Single Site Metallocene Polymers in Full Scale Slurry Loop Reactor". The article points out the different features of the polymers.

In summary if the analysis of the polyethylene reveals for example Cr (for example by atomic spectroscopy) it must be a polyethylene prepared with a "Phillips type" catalyst. Both polyethylene grades are therefore distinguishable.

In view of this, Applicant submits that the 35 USC 102(b) rejections are addressed and are overcome.

Claims 1 and 3-13 are rejected under 35 USC 103(a) as being unpatentable over JP 9193322 in view of Birbaum, et al., U.S. Pat. No. 5,736,597.

Applicant respectfully traverses these rejections.

The limitations of the present claims cannot be met by this combination of references. JP 9193322 does not disclose polyethylene prepared with Phillips type catalyst.

In view of this and the above discussion, Applicant submits that these 35 USC 103(a) rejections are addressed and are overcome.

Claims 1 and 3-14 are rejected under 35 USC 103(a) as being unpatentable over Birbaum '597 or Avar, et al., U.S. Pat. No. 4,891,396 alone or further in view of JP 9193322, Musser, et al., U.S. Pat. No. 4,524,165, Jollenbeck, et al., U.S. Pat. No. 5,498,345, WO 97/39052 or Luethi, et al., U.S. Pat. No. 3,529,982.

Birbaum '597 discloses the combined use of hydroxyphenyl-triazine UV absorbers with sterically hindered amines. Amongst a variety of additives, which may be present in his invention (col. 40, line 48 to col. 42, line 60) Birbaum '597 mentions also other UV absorbers. However, there is no mention of specific UVA combinations or of specific UVA's. There can be no expectation provided from the disclosure of Birbaum '597 towards the synergistic stabilization effect shown in the present invention.

Avar '396 discloses novel benzotriazole UV absorbers for polymers. However, there is no mention of specific UVA combinations or of specific UVA's from which a synergistic stabilization effect could be expected. The skilled person can therefore get no motivation from the Avar '396 disclosure to arrive exactly at the very specific combinations, which show a synergistic effect in polyolefin. Further, there can be no expectation provided as to the success achieved with the present invention.

The synergistic stabilization effects of the present UV absorber combinations in polyolefins is displayed in the working Examples. The synergistic stabilization effects are surprising and could not have been predicted from the disclosures of the cited art.

In regard to the secondary references:

JP '322 has been addressed as discussed above.

Musser '165 discloses specific copolyesterether compositions, which are stabilized with a phenolic antioxidant, a UV absorber and a sterically hindered amine. Musser describes suitable classes of UV absorbers (col. 4 to 6), suitable antioxidants and also suitable sterically hindered amines. There is no mention in the specification that a combination of UV absorbers could have any additional stabilizing effect for these copolyesterethers. Since the invention is directed to specific copolyesterethers, other polymers are not even mentioned. Although example 25 discloses among other components a mixture of a benzotriazole and a benzylidene malonate UV absorber, namely Cyasorb UV-5411 (benzotriazole UVA) Tinuvin 144 (phenolic antioxidant and sterically hindered

amine) Weston 618 (phosphite) and Cyasorb UV-1988 (benzylidene-malonate) there is no teaching for the skilled person to combine exactly those UV absorbers as claimed in the instant invention for polyolefins.

Joellenbeck '345 is directed to a stable aqueous dispersion of a mixture of hydroxybenzophenone UV absorbers and hydroxyphenylbenzotriazole UV absorbers, which is useful for stabilizing colored polyester fibers. The UV absorber dispersion is applied for example together with the dyeing process. These textile applications belong to a completely different field compared to the stabilization of "Phillips type" high density polyethylene. There is therefore no motivation for the skilled person to apply the mixtures of Joellenbeck to HDPE. There is totally lacking the required expectation of success.

WO '052 is directed to the stabilization of polyolefins by a combination of specific sterically hindered amines and a conventional UV absorber. There is no mention of a combined use of UV absorbers in polyolefins. The co-use of UV absorbers is not exemplified.

Luethi '982 describes in 1970 for the first time the use of certain oxalic anilides as effective stabilizers for polymers. This document does not mention any combined use with other classes of UV absorbers.

Applicants submit that the present claims cannot be obvious in view of the primary references cited in these rejections. There is no motivation provided to arrive at the specific stabilizer combinations in polyolefins from the generic disclosures of these references. Further, there can be no expectation of the success achieved with the present invention, that is the synergistic stabilization effect provided for polyolefins.

The secondary references do not rectify the defects of the primary references. JP '322 is moot in view of the present amendments. Musser '165 and Jollenbeck '345 are not aimed at polyolefins and cannot be combined with the primary references to arrive at the present invention. These references further provide no hint towards the synergistic effects achieved with the present invention. WO '052 and Luethi '982 do not mention the combined use of UV absorbers and provide no motivation to do so.

The instant invention discloses and exemplifies the synergistic effect for all claimed combinations. The effect is surprising and cannot be derived from the cited art.

In view of this discussion, Applicants submit that these 35 USC 103(a) rejections are addressed and are overcome.

In view of all of the present amendments and remarks, Applicants submit that each of the 35 USC 102(b) and 35 USC 103(a) rejections are addressed and are overcome.

The Examiner is kindly requested to reconsider and to withdraw the present rejections.

Applicants submit that the present claims are in condition for allowance and respectfully request that they be found allowable.

Respectfully submitted,



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Attachments: Handbook of Polyolefins, edited by C. Vasile and R. B. Seymour, Marcel Dekker  
NY, 1993, ch. 3, pages 21-28

"From Chromium to Single Site Metallocene Polymers in Full Scale Slurry Loop  
Reactor", I. S. Melaaen, 2<sup>nd</sup> International Congress on Metallocene Polymers,  
Metallocenes '96, edited by Schottland Business Research Inc, 1996 page 87-  
95

Markus C. Grob

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# Handbook of Polyolefins

**Synthesis and Properties**

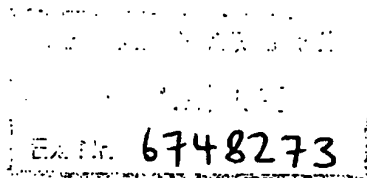
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### 3

## Olefin Polymerization Catalyst Technology

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### I. INTRODUCTION

Olefin polymerization technology as practiced today is an interesting blend of catalyst, process, product, and resin processing developments. One can have the best catalyst and the most economical reactor process and still not have a marketable resin if the resulting material does not satisfy the needs of the resin processor or the specifications of the end user. Conversely, there may be great demand for a process that is only marginally economical, perhaps due to a low activity catalyst, because the resin fulfills the requirements of the marketplace. Therefore, it is not possible in one chapter to cover all aspects of polyolefin technology, even though this would be necessary to give a comprehensive picture. Instead we limit our discussion to the changes that have occurred in polyolefin catalyst technology and attempt to indicate how process, product, or processing changes have resulted from or have been responsible for them.

Transition metal catalyzed olefin polymerizations started with work done both in the United States and in Europe in the early 1950s (see Table 1) [1-3]. Prior to this time polyethylene was produced by a process of Imperial Chemical Industries, Ltd. (ICI), utilizing a peroxide free radical initiator to catalyze the reaction. This process produced highly branched polymers with densities of 0.910 to 0.930 g/cm<sup>3</sup> and became known as the low density polyethylene (LDPE) or high

**TABLE 1** Early Discoveries of Low Pressure Linear Polyethylene

Research group	Catalysts	Time of initial discovery	Early polymer density (g/cm <sup>3</sup> )
Alex Zletz, Standard Oil of Indiana [1]	Nickel oxide on activated carbon Molybdenum oxide on alumina	Early 1950	0.96
J. Paul Hogan and Robert L. Banks, Phillips Petroleum Co. [2]	Chromium oxide on silica alumina	1951	0.95-0.97
Karl Ziegler et al., Max Planck Institute for Coal Research [3]	TiCl <sub>4</sub> + R <sub>3</sub> Al	Late 1953	0.945

\*Retired.



pressure (20,500 psi) process [4]. This process is still in use today, but its share of the total polyethylene market is on the decline.

The early transition metal work resulted in three separate groups of processes: those of Standard Oil of Indiana, Phillips Petroleum, and Ziegler (Table 1). The early catalysts developed by Standard Oil were molybdenum oxide on  $\gamma$ -alumina conditioned or activated before use by treatment with a reducing gas (e.g., hydrogen or carbon monoxide at  $>300^{\circ}\text{C}$ ). Despite the tremendous amount of money spent on development, the catalysts failed to have sufficient activities and the process was soon dropped. No commercial polyethylenes made with molybdenum oxide catalysts are available today.

The Phillips discovery, however, met with a much different fate. In the late 1940s, J. P. Hogan and R. L. Banks were assigned to study the catalytic dimerization and trimerization of olefins, especially ethylene and propylene. The interest in this area stemmed from the large reserves of feedstocks, which could easily be cracked into olefins, held by Phillips. Oligomerization of these olefins might then be used to cheaply produce high octane motor fuels. A catalyst, nickel oxide on silica-alumina, had been developed by Bailey and Reid [5] to accomplish the oligomerization. Catalyst life, however, was only 8–10 turnovers before regeneration. Hogan and Banks added a chromium salt to extend catalyst life. After high temperature air activation of the new catalyst and exposure to propylene, their flow reactor plugged with a solid white material. Although this result was unexpected, the white solid was analyzed and found to contain a unique polypropylene, which was crystalline polypropylene [2]. Within a short time, the new catalysts were used to produce high density polyethylene. Unlike the ICI product, this polyethylene formed with a higher density and at much lower pressures ( $< 1000$  psi).

Phillips did not stop there. Phillips quickly developed a solution process by which to produce this new polyethylene material and began to license it. Within 4 years of the discovery, a Phillips license included a plant design, developmental quantities of polyethylene resin, plant start-up assistance, and a complete information exchange program. This made Phillips the undisputed leader in polyolefin technology for many years and laid the foundation on which Phillips continues among the industry leaders.

The first commercial solution process for the production of polyethylene used a catalyst that consisted of chromium oxide on a silica or silica-aluminum support. The process utilized a volatile hydrocarbon solvent in which ethylene was dissolved. As the polymer formed, it dissolved in the solvent. The catalyst was removed by filtration, and the polymer recovered by precipitation. A process flow diagram is shown in Fig. 1 [6].

The chief competitors to the new resins produced by the Phillips process were those based on the catalysts discovered by Karl Ziegler, who had found that transition metal salts in combination with triethylaluminum (TEA) produced a white solid when reacted with ethylene. Ziegler soon found the most active system to be  $\text{TiCl}_4$  reacted with TEA. He began licensing his technology before Phillips but offered only the catalyst, not process technology. One of the companies to which Ziegler disclosed his new catalyst was Montecatini, which had Professor Giulio Natta as a consultant. Natta recognized the significance of Ziegler's discovery and soon had established a large group of researchers investigating its potential. Natta's work also produced crystalline polypropylene and extended the original discovery in new directions. Because of Natta's contribution to the work begun by Ziegler, catalysts formed by reacting metal alkyls or hydrides with transition metal salts are often referred to as Ziegler-Natta catalysts [7].

This early Ziegler-Natta work was hampered by lack of a convenient method of molecular weight control. Chain transfer to diethyl zinc was found to be effective [8,9], but it was soon learned by people working at Hercules [10] and Montecatini [11] that chain transfer to hydrogen was a much better method of molecular weight control. This feature remains one of the significant differences between the titanium-aluminum alkyl and Phillips polymerization systems. Whereas the titanium-aluminum alkyl system uses hydrogen to control molecular weight, the Phillips sys-

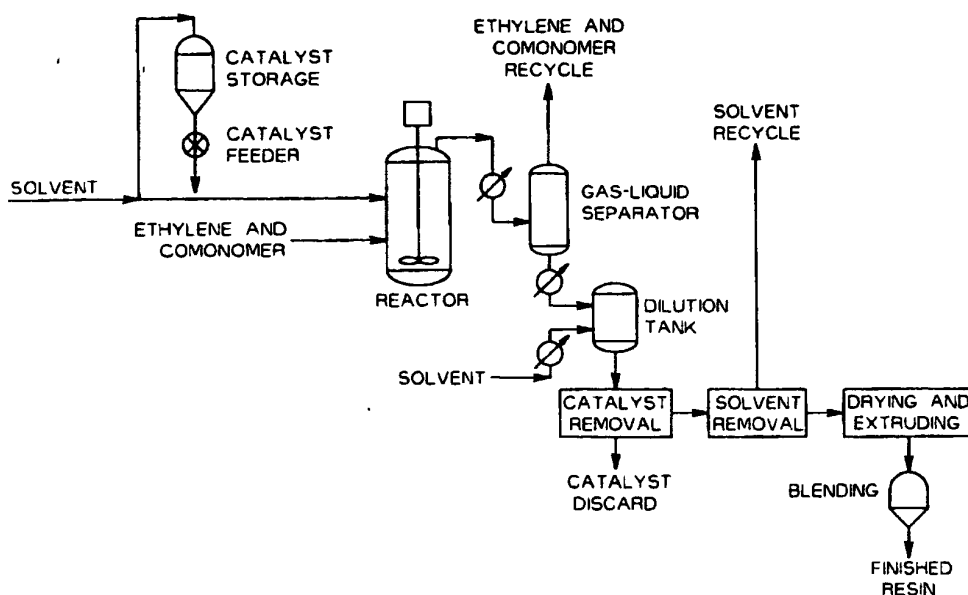


FIG. 1 Flow diagram of the Phillips early solution process. (Reprinted from Ref. 6: *J. Appl. Polym. Sci.: Appl. Polym. Symp.* (N. Platzer, ed.), Interscience—John Wiley & Sons, Inc., 1981.)

tem depends on spontaneous or chain transfer to monomer or comonomer as the main reactions to terminate growing polyethylene chains. For the traditional Phillips catalysts, chain transfer to hydrogen is a very slow reaction and has limited commercial utility.

## II. CHROMIUM CATALYSTS

The typical Phillips catalysts of the 1960s were generally prepared from an amorphous silica gel and  $\text{CrO}_3$ . The  $\text{CrO}_3$  was dissolved in water and the resulting orange solution contacted with a silica support. The silica surface rapidly absorbed the  $\text{CrO}_3$ , 0.5–1.0% chromium by weight, and a dry solid catalyst was obtained by removing the free water. In addition to free water, however, the silica contains bound water, which is present in the form of silanol groups ( $\text{Si—OH}$ ). The free water can be removed by heating to  $100^\circ\text{C}$  or slightly above, but the removal of the bound water requires temperatures up to  $870^\circ\text{C}$  for several hours. These conditions are achieved by fluidizing the silica in a shallow bed with dry air. Bed depth, heating rates, airflow rates, and hold times all influence the final catalyst characteristics, which are to a large extent a reflection of the final water content of the catalyst [12].

In the first solution process these catalysts produced homopolymers and copolymers having a high melt index ( $> 1$  MI), as a result of the high reactor temperatures ( $150$ – $200^\circ\text{C}$ ) required by the process to minimize solution viscosities. Several attempts were made to develop improved catalysts, which would give resins with lower MI values, needed for improved properties, at the higher reactor temperatures. Although new catalysts were developed, the right balance of MI potential and solution viscosity was not achieved to produce resins under 1 MI.

Instead of a catalyst solution, the problem was solved by changing the process. In the new process, called the Phillips loop reactor or particle form (PF) process [13], the catalyst was fed to the pipe loop reactor, which contained a hydrocarbon solvent, *n*-pentane, with ethylene dissolved in it. The polymer then formed on the silica particles as they circulated around the loop.

Intermittently portions of the reactor contents were discharged, the solvent flashed, and the solid fluff particles recovered (Fig. 2). This process was well suited to formation of resins with very high molecular weights. However, in the new PF process MI values were too low ( $< 0.1$  MI). Raising the reactor temperature increased MI values, but temperatures exceeding  $104^{\circ}\text{C}$  resulted in particle swelling and agglomeration with subsequent losses in heat transfer, which led directly to reactor fouling [6].

Two approaches to solving this new problem, one process related and one catalyst related, were pursued successfully. First, other solvents were studied to determine whether the swelling phenomenon occurred at higher temperatures with some solvents. Indeed it was found that isobutane [14] allowed the operating temperature range to be extended to  $111^{\circ}\text{C}$ , was available commercially at a reasonable price and purity, and had a high vapor pressure, which is preferred for direct flash operations.

The second approach to improving MI potential was to modify the catalyst. Chromium contents in the range of 0.5–1.0% depending on catalyst surface area yielded maximum MI values. It was also shown that increasing pore size of the silica increased MI values (Fig. 3) [15]. Not only did MI potential increase, but the activity of the catalyst also increased. Utilizing both the catalyst and solvent improvements, the MI potentials in the particle form process were increased to about 1 MI in some cases.

Still the need for additional MI control, even higher MI values, in the PF process existed. The solution again turned out to be modification of the catalyst. It was soon found that addition of titanyl sulfate to sodium silicate solutions prior to precipitation yielded catalysts containing titania that had additional MI potential [16]. Not only was the MI potential increased to 5–10 MI, but the activity of the catalysts was significantly increased. The nature of the promotional effect of the titania is still not fully understood, but it is thought that  $\text{Ti}-\text{O}-\text{Cr}$  linkages are created which change the electronic environment of the chromium active centers in a manner somewhat analo-

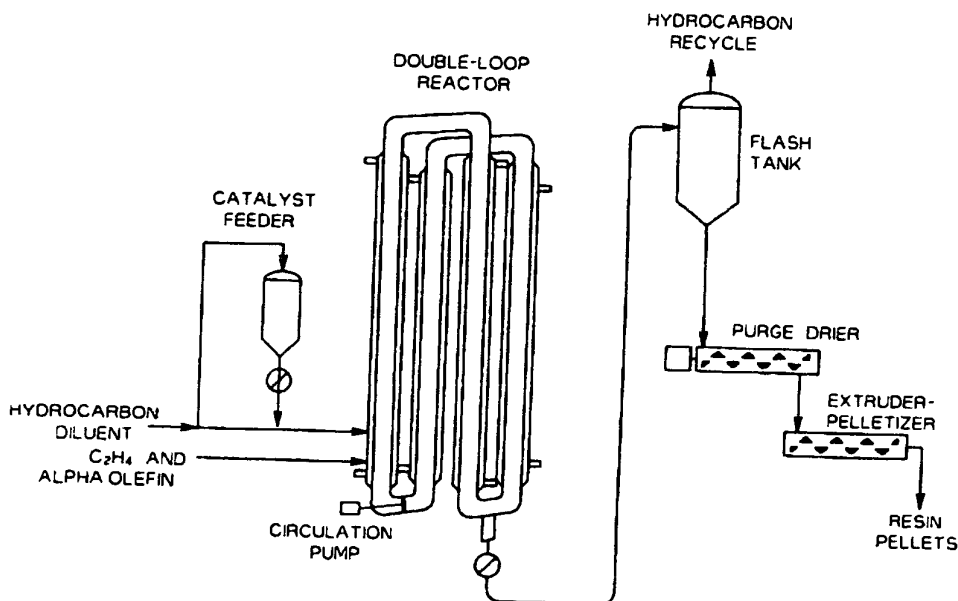


FIG. 2 Flow diagram of the Phillips original loop reactor or particle form process. (Reprinted from Ref. 6: *J. Appl. Polym. Sci.: Appl. Polym. Symp.* (N. Platzer, ed.), Interscience—John Wiley & Sons, 1981.)

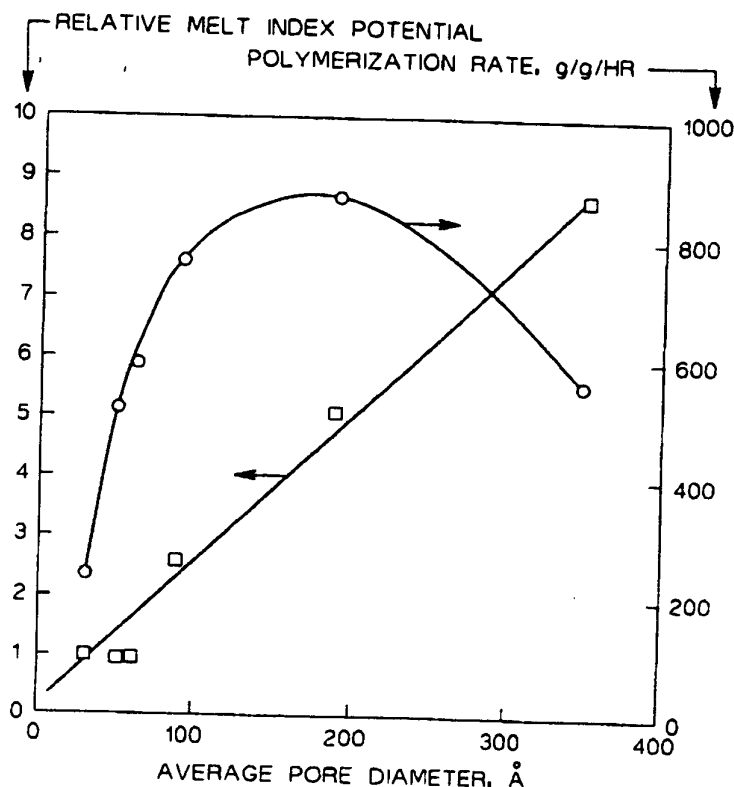


FIG. 3 Effect of silica pore size on relative melt index potential and polymerization rate.

gous to the exertion of influence on MI potentials by the surface hydroxyl population of silica [12]. The proportion of  $\text{Ti}-\text{O}-\text{Cr}$  linkages formed, relative to  $\text{Si}-\text{O}-\text{Cr}$  linkages, is extremely sensitive to subtle variations in the preparation of the catalysts and determines the magnitude of the promotional effects [15].

An alternate method of introducing titania to the catalyst is to treat it prior to activation with a titanium ester [17-19]. This treatment has many of the same promotional effects observed for the coprecipitation method and is more generally applicable to all silicas. However, the two methods of introducing titania do not produce resins with identical properties, and the marketplace has determined the method of choice.

As stated at the beginning, polyethylene technology practiced today is a complicated blend of technology advances. Even though the new titania-containing catalysts offered the higher MI potentials sought, the MI range of products remained constant or perhaps even declined slightly. It was found that these new catalysts offered resins with improved physical properties. A solution to the stated research objective had been found, but the new technology solved other problems that were of far more significance in the marketplace.

At this time there was a booming market in injection molding resins with MI values all greater than 1 and narrow molecular weight distributions (MWDs), to reduce part warpage. Therefore, once again, the research objective was to increase MI values of chromium oxide resins above 1 MI, but this time a new restriction, a narrow MWD, was added.

As already stated, it was well recognized that the drying temperature that establishes the surface hydroxyl population is inversely related to the molecular weight of the resultant polymer

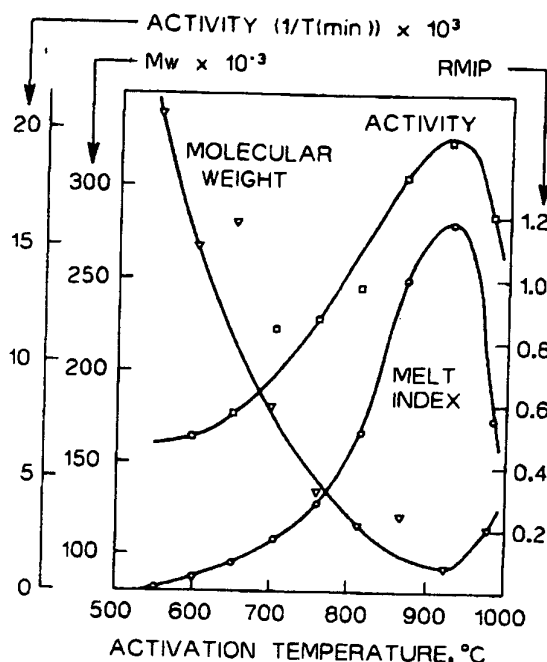
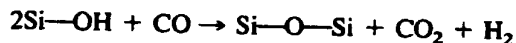


FIG. 4 Dependence of activity, molecular weight, and melt index on activation temperature:  $T$  is the time needed to make 5000 g of polyethylene per gram of catalyst; RMIP is the relative melt index potential. (Reprint from Ref. 20: *J. Catal.* (W. K. Hall and F. S. Stone, eds.), Academic Press, 1983.)

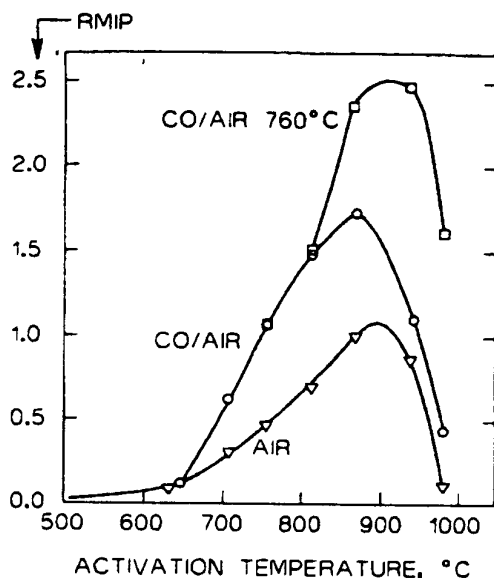
(Fig. 4) [12]. However, the activation temperature was limited by the onset of sintering at 800–900°C. This was a limiting factor in maximizing the MI potential of a catalyst. A means of chemically dehydrating the catalyst surface was therefore needed. It was soon discovered that activation of the catalyst in the presence of carbon monoxide at high temperatures resulted in the desired reduction in surface hydroxyls [20]. This is probably due to the following water gas shift reaction:



Not only did CO treatment chemically dehydrate the surface, it also allowed the use of higher activation temperatures before the onset of sintering, which in turn further dehydroxylated the surface.

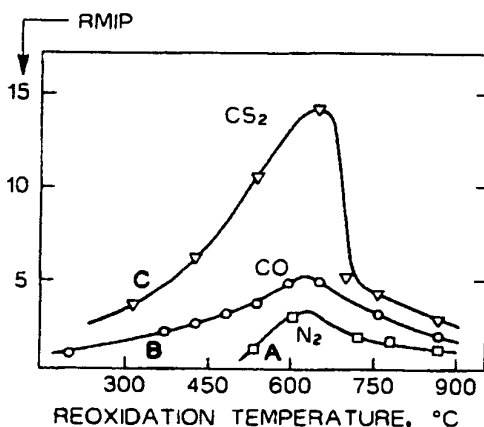
By itself, this treatment of the silica surface in a reducing medium at high temperatures (> 800°C) would result in a dead or extremely low activity catalyst. Such loss in activity probably results from rearrangement or migration of the surface chromium species into surface aggregates that have little activity. These aggregates, however, can be redispersed on the silica surface by reoxidation in air at lower temperatures. These catalyst features are shown in Fig. 5 [20]. The lower curve represents a standard air activation. The middle curve shows the results of CO activation with air reoxidation at the same temperature. Maximum MI potential, however, was realized in the upper curve by CO reduction at the indicated temperature followed by air reoxidation at 760°C. Thus, the middle and upper curves can vary only in the way that the chromium is redistributed on the surface of the silica.

Further increases in MI potential using the reduced and reoxidized (R&R) techniques just described are found if a sulfur compound such as carbon disulfide is used. This is shown in Fig. 6 [20]. One must be careful, however, because sulfur at high temperatures can result in severe



**FIG. 5** Relative melt index potential of modified silica catalysts activated in air for 5 hours at temperature shown, in CO for 3 hours then in air for 2 hours at temperature shown, and in CO for 3 hours at temperature shown, then in air for 2 hours at 760°C. (Reprinted from Ref. 20: *J. Catal.* (W. K. Hall and F. S. Stone, eds.) Academic Press, 1983.)

activator metal fatigue. In addition, nitrogen alone can be used in the R&R technique to increase MI potentials. Nitrogen does not chemically dehydroxylate the surface but it does reduce the chromium species, resulting in aggregates of chromium that can be redispersed on the surface with a low temperature oxidation as shown in Fig. 6, in analogy with the CO R&R techniques.

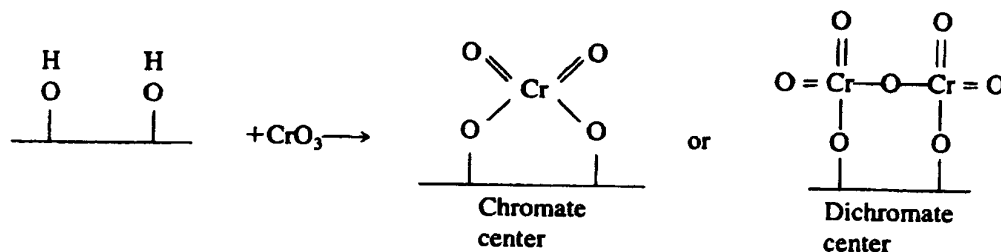


**FIG. 6** Samples of Cr/silica-titania were calcined at 870°C in (A) N<sub>2</sub>, (B) CO, or (C) N<sub>2</sub> with CS<sub>2</sub> vapor. Then each was reoxidized in dry air at the temperature shown. (Reprinted from Ref. 20: *J. Catal.* (W. K. Hall and F. S. Stone, eds.), Academic Press, 1983.)

Once again the research objective of higher MI potential was achieved by catalyst developments, but the MWDs of the resulting polymers were still broader than the corresponding titanium–aluminum alkyl systems. In addition, simultaneous discoveries in the titanium–aluminum alkyl area greatly improved these catalysts and made them very attractive commercially.

This resulted in the use of chromium oxide resins for applications in which their broad MWDs provided the necessary processing and physical properties, and in the use of titanium–aluminum alkyl resins for applications in which the narrower MWDs provided low warpage. With few exceptions this division in applications for the two catalysts existed from the early 1960s through the 1980s.

The two most controversial issues surrounding the Phillips chromium oxide catalysts have been the oxidation state of the chromium polymerization center [21–30] and the question of whether the active site originates from chromate or dichromate centers, as follows [21,22,31]:



The most recent work by McDaniel and coworkers [32–35] at Phillips suggests the following view of the catalyst. The active center precursors consist of isolated chromate and perhaps dichromate species, which in the presence of ethylene are reduced to the divalent, highly coordinatively unsaturated form.

Other chromium catalysts for ethylene polymerization have been developed and described. For example, Ballard obtained highly active catalysts by supporting  $\pi$ -allyl chromium [36]. Union Carbide developed chromocene [37] and silyl chromate [38] catalysts. Phillips has also continued its quest for new catalysts and has a new series based on aluminum phosphate containing base materials developed by McDaniel and Johnson [39, 40]. In addition, new mixed valence states of chromium on a single support have been used to generate both comonomer and polymer on the same catalyst particle [41].

These results make the chromium oxide catalysts developed at Phillips the most versatile ethylene polymerization catalysts on the market today. One can achieve broad molecular weight distributions, high melt indices in the particle form process, exceptional comonomer incorporation efficiencies, and a very wide range of resin physical properties by simple modification of the catalyst or activation conditions.

### III. TITANIUM–ALUMINUM ALKYL CATALYSTS

Initially the use of titanium–aluminum alkyl catalysts to produce polyethylene grew at a much slower pace than the chromium oxide on silica catalysts. The main difficulty with the original catalysts was that the yield of polymer per unit of catalyst in low pressure processes was so low that the catalyst residuals in the polymer had to be extracted. Typical yields of some of these early catalysts were under 5 kg of polyethylene per gram of transition metal, which resulted in titanium residuals as high as 100 ppm. Not only were titanium residuals high but chloride levels were correspondingly high, resulting in severe corrosion problems in addition to the color and stability problems caused by the metal residuals. The only way to avoid these problems was to remove these entities from the polymer, using expensive wash columns and adjuvants such as propylene oxide. Since chromium oxide catalysts were high in activity (200–600 kg of polymer per gram of

TABLE 2 Early Supported Catalysts

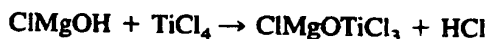
Patent no.	Date	Company	Catalyst preparation
BP 841,822	1955	British Petrochemicals	TiCl <sub>4</sub> reduced by aluminum alkyls in the presence of solids such as MgCO <sub>3</sub>
U.S. 3,153,634	1956	Sun Oil	TiCl <sub>4</sub> was adsorbed on SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> and reduced
U.S. 2,980,662	1956	Sun Oil	Ti compounds reduced in the presence of solid NaCl, FeCl <sub>3</sub> , AlCl <sub>3</sub> , GaCl <sub>3</sub> , etc.
BP 877,457	1957	Sun Oil	TiCl <sub>4</sub> reduced in the presence of inorganic compounds
BP 969,761	1960	Cabot	Transition metal compounds reduced in the presence of SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> , TiO <sub>2</sub> , ThO, MgO, etc.
BP 969,767	1963	Cabot	Transition metal compounds reduced in the presence of SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> , TiO <sub>2</sub> , ThO, MgO, etc.

Cr metal) and contained no chloride, no catalyst residual removal steps were required. Thus, the cost of operating a titanium–aluminum alkyl process exceeded that of operating a Phillips process. Yet, the market demand for a low molecular weight, narrow MWD resin was sufficient to spur research [42].

Here is a good example of how catalyst, process, and market interact. In the early 1970s the Phillips slurry process with Phillips catalyst was less costly and easier to operate. However, some products demanded by the marketplace could not be efficiently produced. So without promise of success, research on the titanium–aluminum alkyl catalysts to improve activities continued at a rapid pace. In the end these efforts were very successful, and the marketplace today is supplied with the sought-after titanium–aluminum alkyl resin from processes (slurry, solution, and gas phase), which are much more economical than the earlier versions.

The advance in titanium–aluminum alkyl catalysts resulted from efforts to form supported catalysts on a variety of materials. Although many of these new supported catalysts no longer consisted of titanium tetrachloride or trichloride and aluminum alkyl or alkyl halide alone, the active centers were similar. Table 2 shows some of the initial work on supported early transition metal catalysts. Although the patented processes represented here did not accomplish the goal of eliminating catalyst removal process steps, they did point the direction and provide the needed incentive to continue the efforts. Notice how early the supported work began: 1955. The first supports were metal oxides (perhaps an imitation of chromium oxide successes), halides, and carbonates.

In the mid-1960s the work on these transition metal supported systems really began to reach fruition. Possibly stimulated by Cabot's 1960 patent (BP 969,761) Solvay, Hoechst, Mitsui, Montecatini, and B. F. Goodrich came out with a series of patents dealing with supporting halotitanium species on hydroxymagnesium halides (Table 3). The degree of dehydration of the support, just as with chromium–silica catalysts, played a significant role in their activities. The small average particle diameters and relatively high specific surface areas also helped to produce optimum results. However, the precise structural features of the support in promoting the desired polymer yield and properties were never clearly defined as they were for the Phillips catalysts. The accepted reaction of the transition metal halide with the support is:



While the researchers just mentioned were studying the classic supported catalyst approach with transition metals attached to surface hydroxy species, other groups were finding that the transition metal did not have to be anchored to the support for high activities. Many of these catalysts (Table



**TABLE 3** Magnesium Hydroxychloride Supported Catalysts

Patent no.	Date	Company	Catalyst preparation
BP 1,024,336	1963	Solvay	Reaction of a transition metal compound with a hydroxychloride of a bivalent metal, preferably $\text{Mg}(\text{OH})\text{Cl}$
JP45-40295	1967	Mitsui	$\text{TiCl}_4$ reacted with $\text{Mg}(\text{OH})_2$ and reduced
U.S. 3,634,384	1968	B. F. Goodrich	$\text{TiCl}_4$ reacted with $\text{Mg}(\text{OH})_2$ and reduced
BE 726,839	1968	Solvay	Reaction of magnesium hydroxide with a transition metal halide.
BE 728,002	1968	Montecatini	
BE 735,291	1968	Hoechst	

4) consisted of magnesium alkoxides reacted with transition metal halides. During the preparation, the original structure of the magnesium alkoxide is completely destroyed and a new species formed, perhaps with an increase in surface area. These catalysts could be further modified by introduction of additional compounds into the catalytic complexes such as complex magnesium alkoxides (e.g.,  $\text{Li}_2[\text{Mg}(\text{OC}_2\text{H}_5)_4]$ ) or by carrying out the reactions in the presence of an acid halide (e.g.,  $\text{SiCl}_4$  or  $\text{BCl}_3$ ). By the end of the 1960s, there was a good deal of interest in this new type of catalyst, which no longer required expensive deashing steps.

Gradually evolving from all this concentrated titanium-aluminum alkyl catalyst research were even higher activity catalysts. These supported approaches eventually led to the catalyst systems consisting of  $\text{MgCl}_2$  ball-milled with  $\text{TiCl}_4$ . Interestingly, the ball-milling approach used to form these supported catalysts was analogous to the activation step for  $\text{TiCl}_3$  propylene polymerization catalysts in use at that time. This is a good example of the way that success in one area of catalysis can significantly influence new approaches in another area. It was also a well-established practice to modify propylene polymerization catalyst activities and stereoregularities with Lewis bases. Therefore, it was reasonable to try to combine the newly ball-milled  $\text{MgCl}_2 \cdot \text{Mg}(\text{TiCl}_4)$  catalysts with alkoxides similar to those used for the  $\text{Mg}(\text{OR})_2 \cdot \text{TiCl}_4$  system. The results by the early 1970s were yet another boost in catalyst activity, which was at this point high enough to eliminate all deashing steps (Table 5).

Ball-milling steps can be messy, expensive, and very energy intensive. They also tend to produce very fine polymer particles, which are difficult to handle in a polyolefin plant environment. Thus research on ways to produce these new catalysts without the ball-milling step continued.

By the mid-1970s a new process, gas phase [43-47], had entered the scene as a major player, further increasing the demands on the catalysts. No longer were high activity and low fines sufficient. Now it became desirable to carefully control fluff morphology and catalyst kinetics to ensure the controlled operation of gas phase processes. The new process, at first, did not make high quality HDPE resins well. However, the demand for a new linear low density polyethylene (LLDPE) was growing, and the new process was soon debugged to efficiently produce these new resins.

**TABLE 4** Magnesium Alkoxide Based Catalysts

Patent no.	Date	Company	Catalyst preparation
U.S. 3,644,318	1968	Hoechst	$\text{TiCl}_4$ reacted with $\text{Mg}(\text{OR})_2$ or a complex magnesium alkoxide
BE 758,994	1969	Hoechst	
BE 743,325	1969	Solvay	
BE 780,530	1971	Hoechst	Reaction of magnesium alkoxide and an acid halide with a tetravalent titanium compound
NL 216,195	1971	Solvay	

TABLE 5 Magnesium Chloride Based Catalysts

Patent no.	Date	Company	Catalyst preparation
BP 1,286,867	1968	Montecatini	TiCl <sub>4</sub> ball-milled with MgCl <sub>2</sub>
BE 744,221	1969	Montecatini	Reaction of MgCl <sub>2</sub> with halogenated
BE 747,846	1969	Montecatini	titanium compounds
JP 46-34092	1968	Mitsui	TiCl <sub>4</sub> reacted with MgCl <sub>2</sub> · <i>n</i> ROH or
U.S. 3,642,746	1968	Mitsui	MgCl <sub>2</sub> · <i>n</i> H <sub>2</sub> O or MgCl <sub>2</sub> ·Lewis base
JP 46-34093	1968	Mitsui	
BE 755,185	1969	Hoechst	Reaction of a magnesium dihalide electron donor adduct (e.g., MgCl <sub>2</sub> ·6C <sub>2</sub> H <sub>5</sub> OH) with a titanium compound

The low densities demanded by the new market created yet another catalyst challenge, one that still continues. Ideally the 1-olefin comonomer, used to lower the density, would have a rate of polymerization comparable to the rate of polymerization for ethylene. This would minimize process problems, including recycle and residual fluff volatiles. However, the rates for 1-olefin incorporation into the growing chain on a titanium-aluminum alkyl polymerization center are significantly slower than rates for ethylene, which leads to high reactor 1-olefin concentrations and resulting process problems. The challenge is to find new titanium-aluminum alkyl catalysts that incorporate comonomers at faster rates. The literature in this area is very confusing because it is difficult to determine comonomer incorporation efficiencies from bench scale experiments. Moreover, many improvements are marginal, and there is no universal standard set of reaction conditions, with the result that each researcher selects his own set of reaction conditions at which to conduct comparative studies.

Comonomer incorporation efficiencies are related to process problems, but it is the properties of the final resin that make it marketable. The end-use properties of copolymers are controlled by three factors: the type of comonomer used, the percentage of comonomer in the resin, and the distribution of the comonomer, both intra- and intermolecular, which in turn is affected by catalyst and process conditions. The first two factors are easily controlled by adjusting the type and level of the comonomer in the reactor, but this control is complicated by the fact that different comonomers impart relatively different effects on properties depending on the final resin density.

The homogeneity of comonomer incorporation, however, is much more difficult to control or even measure. A new analytical technique called *temperature rising elution fractionation* (TREF) has been developed just to deal with the homogeneity of short chain branching [48-51]. The technique consists of crystallizing a solution of polyethylene in a hydrocarbon at very slow cooling rates (1.5°C/h), with or without a high surface area support material present. This allows separation of the molecules based on molecular weight and crystallinity. The temperature is then raised, and the polymer is eluted at different temperatures according to these same parameters.

When applied to linear lower density polyethylene, this technique gives spectra typified by Fig. 7. The bimodal nature of the spectrum suggests that some polymerization sites incorporate little or no comonomer, giving rise to the 90-100°C peak, while other sites incorporate comonomer readily (the 70-80°C peak). This suggests that two resins can have identical chain lengths, degrees of branching, and densities but differ significantly in end-use properties because of the heterogeneity of comonomer incorporation. Production of polymers with a more homogeneous distribution of the comonomers would be preferred and should lead to improved physical properties.

As plants reach their full capacity and "debottlenecking" projects further increase capacity, another catalyst-related issue, bulk densities, becomes increasingly important. By minimizing the

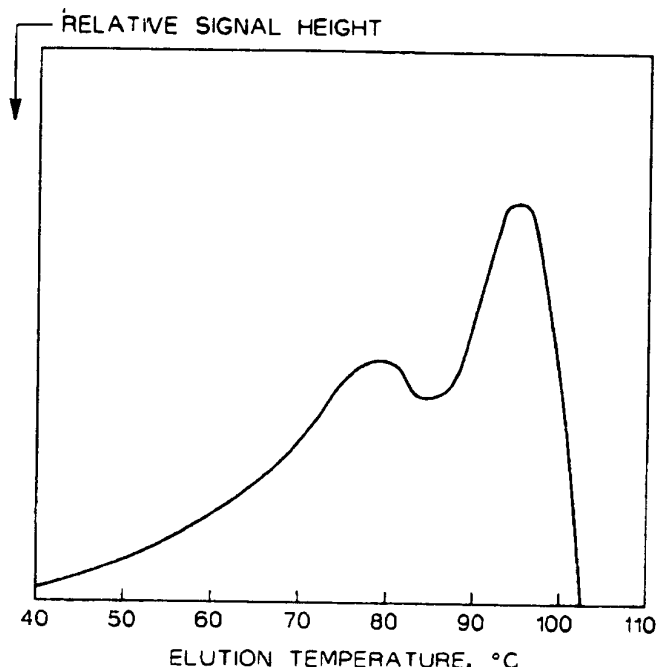


FIG. 7 Typical TREF results for a linear low density polyethylene.

volume of the solid material in a reactor, even more material can be produced per unit volume. Thus the fluff bulk density becomes a critical issue. The catalyst manufacturing technique, again, can influence this parameter.

All these new demands on the catalyst have required further refinements and sophistication of the catalysts. The ball-milled supported  $\text{MgCl}_2$  catalysts have been replaced with new unsupported systems, which address many of the new catalyst constraints. Methods of forming these new catalysts consist either of precipitating dialkylmagnesium or alkylmagnesium chloride from hydrocarbon solution, or of precipitating a hydrocarbon solution of a Lewis base and magnesium dichloride [52–55]. The (titanium) specimen can be added before, during, or after the precipitation. The latter technique, which often consists of a  $\text{TiCl}_4$  contacting step, is frequently preferred because it maximizes activities.

The early focus was solely on catalyst productivity, but now fluff bulk density, fluff morphology, fluff fines, catalyst kinetics, catalyst handling characteristics, and comonomer incorporation efficiency are just as important. The successful commercial catalysts of today are those that address many of the foregoing issues and offer compatibility with the process to be used.

#### IV. FUTURE TRENDS IN ETHYLENE POLYMERIZATION

##### A. Catalysis

The past has amply demonstrated that the future cannot be forecast with much certainty, but certain trends can be identified. The most obvious industry trend is the push toward multimodal-type resins [56–59]. This work begun back in the 1960s at Phillips by W. M. Nelson [56], is just now reaching fruition. By blending resins of vastly different molecular weights and comonomer contents, the production of resins with an exceptional balance of stiffness, toughness or environ-

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Aluminoxane catalysts appear to be well suited to production of these syndiotactic polypropylenes. Also, new catalysts are being investigated for random and block copolymers.

## V. CONCLUSIONS

Olefin polymerization technology has progressed tremendously in the past 40 years. Today's resins, however, must meet the requirements of new high speed process equipment while providing increased properties and toughness. Environmental and economic concerns have dictated that these improvements be achieved while simultaneously decreasing the amount of resin used for a given product. Today's commercial polymerization processes are more demanding as well, as a result of the ever-increasing pressure to increase space-time yields and to lower other manufacturing costs. Thus, the need for catalyst innovations is even greater today than it was 40 years ago.

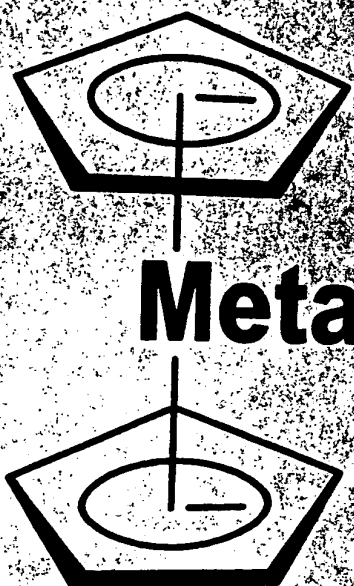
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**FROM CHROMIUM TO SINGLE SITE METALLOCENE POLYMERS  
IN FULL SCALE SLURRY LOOP REACTOR**

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## ABSTRACT

A proprietary single site metallocene catalyst has been developed in Borealis, Finland.

During the first week of December 1995, this catalyst was used in a successful full scale metallocene trial in our 130 ktons/year LPPE slurry loop reactor plant in Norway. Several hundred tons of medium density polymer were produced with good production economy and high production rates.

This technology makes us able to produce single site polymers with narrow molecular weight distribution and densities from 915 to 945 kg/m<sup>3</sup>.

This paper will present the implementation of single site metallocene catalyst from bench scale via pilot plant to a full scale LPPE slurry loop reactor plant.

## 1. INTRODUCTION

Borealis is the largest polyolefin producer in Europe and the 5th largest world wide. In these days, the company could celebrate its 2nd year anniversary. It is owned half by Finnish Neste and half by Norwegian Statoil.

Single Site Catalyst (SSC) development started in 1992 in Finland. Bench scale experiments for polyethene polymerisations were performed during the next years while the catalyst was gradually developed for slurry reactors.

The scale-up work for slurry loop reactors started by a successful pilot trial during two weeks in summer -94 for medium density products. Later, we performed two full scale test runs in the first half of 1995. Through these two runs we obtained confidence in flying transitions from Chromium to SSC and production product properties concerning density and melt flow rate. Our third commercial test run in December -95 made us able to make the same products with good production economy. In the mean time, we have also performed a pilot test run on LLDPE products down to 915 kg/m<sup>3</sup>.

The differences in producing the different polymers are reflecting the generally known inequalities between Chromium catalyst and SSC that are presented in Table 1.

*Table 1: Differences in Chromium and SSC performance*

Chromium catalyst	SSC
All active sites are different ↓	All active sites are nearly equal ↓
All polymer chains are different ↓	All polymer chains are nearly equal ↓
Broad molecular weight distribution Hexene is unevenly distributed (Mostly on short chains)	Narrow molecular weight distribution Hexene is evenly distributed (On all chains)

Different polymer properties are mainly due to the difference in molecular weight distribution and the distribution of hexene on the chains.



## 2. SCALE-UP

The commercial Phillips loop reactor process for polyethene polymerisation consists mainly of five main steps

1. Purification of reactants (ethene, hexene, hydrogen) and diluent (isobutane)
2. Polymerisation in liquid diluent
3. Separation of fluff from diluent and excess monomer
4. Drying of fluff
5. Pelletising

Before even thinking of scale-up, the catalyst itself has to satisfy several process demands. It has to be completely insoluble in isobutane, control fluff morphology, keep the high heat transfer coefficient by maintaining low slurry viscosity, reduce formation of small soluble polymer that could cause reactor fouling, and of course, produce the wanted polymer with a productivity at a commercial level. Scale-up was decided when the catalyst was able to give satisfactory results in all these areas.

During scale-up, it is important to utilise the relevant information that is obtainable on each stage, and be aware of eventually misleading results that can appear because of the insufficiency of the method and system applied.

Main differences between laboratory, pilot and full scale are

- ⇒ Volume, complexity and amount of equipment
- ⇒ Feeding systems (continuously or batchwise)
- ⇒ Product treatment (separation of fluff and diluent, pelletising)
- ⇒ Safety limits
- ⇒ Number of people involved

### 2.1 Laboratory

Laboratory experiments are mainly performed in small bench scale reactors with batchwise addition of catalyst, isobutane, hexene and hydrogen. Ethene is added continuously. Reactions were tested over a wide range of temperatures and hexene, ethene and hydrogen levels.

Results from bench scale show that our wanted polymers can be made from our SSC, they show the ranges of concentrations for reactants and reactor temperature limits, indicate tolerable poison levels, reasonable productivity levels and show fluff morphology.

### 2.2 Pilot plant

A pilot plant is necessary especially if larger changes are to be done with a commercial plant as for instance to change catalyst system from Chromium to SSC. First of all from the process point of view, it can show the feasibility of doing the polymerisation in a fully continuous system, that not impurities are accumulating in the reactor, and that the applied construction materials can be used. And, because the feeding systems are much more equal to the commercial plant, we can obtain more exact information about concentrations needed. From polymer development viewpoint, it is just as important that the pilot can produce material for evaluation and eventually introduction to the market. Another benefit is that a successful trial in pilot can give the necessary support for investments in the commercial plant. At last, but not at least, the number of overlookings or misinterpretations of important factors ahead of a full scale test run can be reduced.

The slurry loop pilot plant in Borealis has a capacity of a 30 kg/h, and consists mainly of a single loop and a large flash drum. Additions of all reactants and diluent are continuously, and product outtake is similar as in a commercial plant. Some mathematical models have been applied to convert reactor conditions from bench scale polymerisations to the pilot plant. In pilot, it has been produced products in the density range from below 915 to 945 kg/m<sup>3</sup>. Here, we have experienced productivities up to the level of 10 tons/kg catalyst.

### 2.3 Commercial plant

Our commercial low pressure polyethene plant in Norway where SSC is scaled up, has a double loop reactor with a nominal capacity of 130 ktons/year.

Just when seeing the units of the feed input parameters to the plant that are given in kg instead of mole, this is reflecting a major difference between laboratory and pilot compared to full scale. Here is the main goal to produce tons of product and not fine tune molar compositions. Pilot plants are build for testing, but full scale plants are build for producing commercial volumes. Commercial test run time reduces commercial production time and therefore the probability for success has to be higher when you start commercial test run compared to pilot. The larger volumes in the plant also imply more detailed safety work.

Laboratories and pilot plants are generally more flexible than a commercial plant. They are built for testing different types of catalyst systems, and for each system, they should be able to scan wide ranges both in concentrations, pressure and temperature. Measurement instruments and controllers are constructed to satisfy very different needs. This also holds for purification systems. For a commercial plant it is expensive to have equipment that is oversized. Sometimes, investments of new equipment can delay or even stop a scale-up even if it is technically possible.

Compared to the pilot plant, the main construction difference is that the full scale plant has recycling of diluent. It can be difficult to simulate this recycle and completely eliminate any problems in this part of the plant. There is always a possibility that some catalyst poison can be accumulated in the recycle diluent especially if this poison has its boiling point limits near the boiling point of the diluent.

Plant production capacity is mainly restricted by feed systems and cooling capacity of the reactor. This cooling capacity is given from the heat transfer area, heat transfer coefficient and the temperature difference between cooling water and reactor temperature. In our full scale reactor, the heat transfer coefficient is very high and the most easy way of increasing the cooling capacity at a given reactor temperature is then to reduce the wall temperature. Too cold wall temperature can give freeze out of polymer on the wall immediately followed by reduced heat transfer coefficient and plugging of the reactor. Finding this lowest possible wall temperature is difficult with a pilot plant that has not the similar geometry concerning volume/heat transfer area and similar slurry flow profiles.

It is important both from health and security reasons to keep the hydrocarbon level as low as possible in the polymer fluff. Fluff treatment is therefore also more sophisticated in a full scale plant than in a pilot. The fluff is dried in an electrical drier succeeding the flash drum, and then purged with hot nitrogen.

Extrusion has not been scaled up in the same way as the reactor conditions because the pilot extruders are not comparable to the full scale one.

The organisation of a commercial plant do need some extra support during such large test runs, both in the process area and at the quality control laboratory. The intensity of taking test samples has to be high during commercial test run to really follow up what is happening, and especially, if what is happening in the plant is very different from what was supposed. Full scale runs are dependent on detailed test run instructions in the same time that all people involved have to be aware of that it is not 100% sure that what will happen in the full scale is equal to extrapolations from bench scale and pilot plant experience. People who are running the full scale plant have to be well instructed and prepared to do improvisations all the time.

### 3. FULL SCALE SINGLE SITE POLYMER PRODUCTION

The intention of the test run was to produce a saleable polymer with good production economy based on Borealis own single site metallocene catalyst in full scale slurry loop reactor.

#### 3.1 Preparation of the plant

Catalyst was produced in Finland and shipped to Norway a few weeks ahead of the test run.

In the mean time, a production group that consisted of process development engineers, plant engineers and operators examined the plant in detail for preparation of the introduction of the new catalyst. Hazard and operability analysis (HAZOP) were also performed since the SSC can be pyrophoric.

A detailed test run instruction was written.

Bench scale polymerisations were then performed at the laboratories with the same raw materials and purifiers as were used in the plant. Analysis and material laboratories were calibrating their methods for analysing the single site polymer.

All shift personnel and day-time employees in the plant had a two hours course in SSC performance. The planned progress of the test run was also examined. During the test run each shift was extended with two to three operators, and a process development engineer. Quality control laboratory shifts were also extended with two more engineers at each shift.

#### 3.2 Transition from Chromium to SSC

Since Chromium products are usually produced in the plant, we had to apply a special transition to SSC based polymers. There are two philosophies concerning transition from one product to another;

- ⇒ Kill existing polymerisation process, empty reactor and start again on the new product
- ⇒ "Flying" transition where the change from one polymer to another is continuously

A benefit with the first transition procedure, is that the rest material from the beforehand run will be less in the plant. A disadvantage is that it takes several hours to build up a desired level of solids in the reactor. Additionally, it will always be traces in the rest of the process equipment which will be impossible to clean between each grade. This has to be pushed away with new material.

In the low pressure polyethene plant, we always do flying transitions from one grade to another to reduce the transition time to a minimum. For this test run, we decided to do flying transition from a Chromium polymer with about the same hexene level as the first single site polymer. One full mud pot of SSC was needed for the test run. This SSC can be fed into the

reactor in the same way as Chromium catalyst, but it was necessary to modify our feed system from the catalyst containers to the mud pots. We had to be sure that the new reactor conditions for the single site catalyst were not too unfavourable for Chromium, so that for instance high molecular weight Chromium polymer could not give problems into the extruder. The transition was followed up by IR-measurements to see when the plant was free from Chromium based polymer. The amount of Chromium was reduced to ten percent after five hours, and it took additionally four hours until the system was completely free from Chromium polymer. During this transition, the average rate was 10.5 tons/h. Figure 1 shows the change in melt flow rate ratio during the corresponding decrease in Chromium content in fluff. This melt flow rate ratio stabilised at about 15 four hours after the first SSC injection.

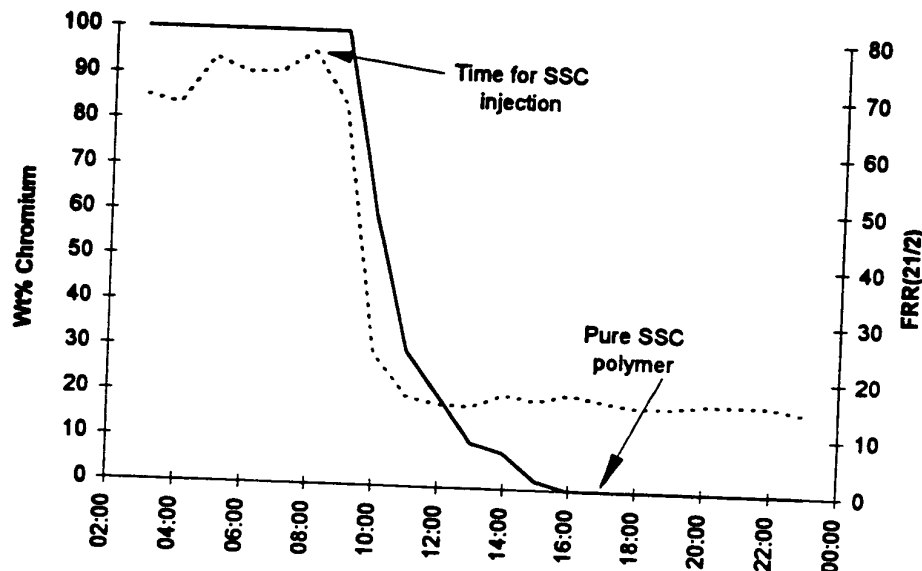


Figure 1: Transition period from Chromium to SSC polymer

Flying transition back to chromium subsequent to SSC went much faster. This can be due to the different shape of the fluff particles. It is believed that the Chromium polymer flakes stick much more to the walls than the spherical shaped fluff from SSC, and is therefore more difficult to remove.

### 3.3 Production of target properties

To produce a given resin commercially, the catalyst productivity has to be higher than 2 tons/kg catalyst to satisfy customer demands, and even higher to satisfy economical demands. When reactor parameters were specified, all parameters were optimised both with respect to productivity and product properties. As already known, the hexene incorporation is much more uniform in SSC polymers than in Chromium polymer. This leads to the need for smaller amounts of hexene for the same polymer density. Melt flow rate is corrected by hydrogen and to a certain degree by ethene. Reactor temperature is not highly optimised for these products yet. It is supposed that the limit for swelling is at a higher reactor temperature than for Chromium because of the more narrow molecular weight distribution.

From the operator point of view, one of the major differences between running Chromium and SSC polymer is that the induction time is very short for SSC. Changes in reactor parameters gave much faster response on changes than for Chromium catalyst.

We did also observe that static coating at the reactor walls was somewhat more easily created than for Chromium catalyst, but this was no problem to handle by a small increase in dosage of anti static agent.

Fluff morphology is very good. Very small amounts of fines were observed and this is very beneficial during filtering of overhead gas phase from flash drum. Figure 2 shows a comparison between cumulative particle size distribution for our two products (SSC-1, SSC-2) and one high density (Cr-HD) and one medium density (Cr-MD) Chromium polymer.

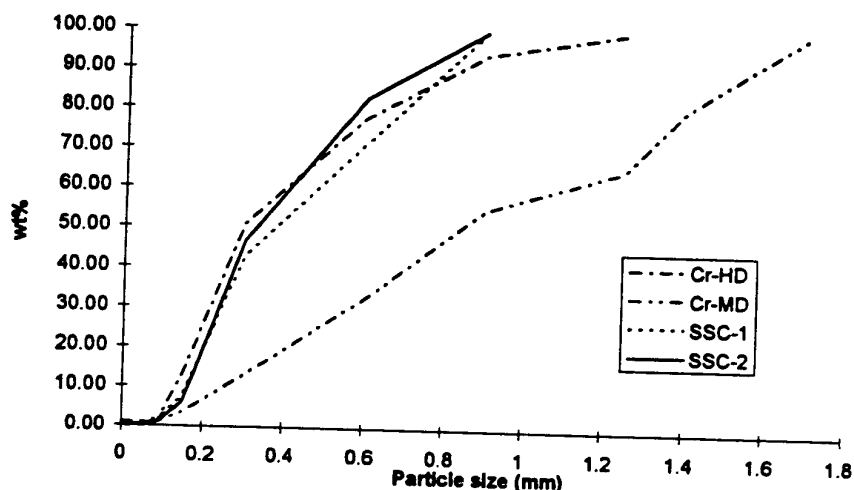


Figure 2: Cumulative particle size distribution

It was no problem keeping high solid content in the reactor and the average level was at 36.5 wt%. Average settling efficiency was 52 wt%. Without pushing the reactor we reached a polymer production rate of 13.5 tons/h.

It is important to keep the temperature in the flash line and flash drum as high as possible and the pressure as low as possible to remove the hydrocarbon gas from the fluff particles. We used steam on the drier to increase amount of hydrocarbons leaving the fluff in addition to hot nitrogen in the purge tower. No problems with high hydrocarbon level in fluff were observed.

Extrusion of single site polymer is very different from extrusion of Chromium polymer because of the narrow molecular weight distribution. The flow properties are more independent of processability, and then the viscosity curve with respect to shear rate is more flat. Suitable amounts of lubricants are necessary to obtain stable operation. The extruder was running continuously at stable conditions during the test run and reached a maximum rate of 14.8 tons/h.

### 3.4 Production economy

For the medium single site polymers produced during this test run, the production economy was quite as good as for Chromium polymer.

Conversion of monomer is at the same level as for usual Chromium production. For a given density, we have observed less comonomer consumption as for a corresponding density Chromium polymer. Because of better conversion of comonomer, the amount of comonomer loss in the recycle system is less than usual. Catalyst activity has been at the same level as Chromium catalyst even for these medium density SSC polymers with fairly low hexene level. The catalyst is more expensive, but the price is still decreasing. Additives are still more expensive, but the recipes are not optimised yet.

### 4. CONCLUSION

Borealis has performed their first successful full scale test run for medium density single site metallocene catalyst in slurry loop reactor. Several hundred tons of two different products were produced at good production economy. Catalyst development and scale-up work from laboratory via pilot to commercial scale have been done totally within the company.

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36.5 wt% solids in reactor  
13.5 t/h production  
more anti-static agent needed (well coating!)